



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US93/02167 <b>(22) International Filing Date:</b> 16 March 1993 (16.03.93)  <b>(30) Priority data:</b> 872,869                      23 April 1992 (23.04.92)                      US  <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US    872,869 (CON) Filed on                                      23 April 1992 (23.04.92)  <b>(71) Applicant (for all designated States except US):</b> PFIZER INC. [US/US]; 235 East 42nd Street, New York, NY 10017 (US).		<b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> REIMER, Robert, A. [US/US]; 10 Forest Lane, Gales Ferry, CT 06335 (US). CARRUTHERS, Mark, S. [US/US]; 2 Willowbrook Farm Road, Old Saybrook, CT 06475 (US). CORR, Ro- bert, J., Jr. [US/US]; 77 Montauk Road, Charlestown, RI 02813 (US). MILLER, James, W. [US/US]; 39 Bar- ton Lane, Ledyard, CT 06339 (US). TARLTON, Eugene [US/US]; 107 Witter Road, Salem, CT 06420 (US).  <b>(74) Agents:</b> RICHARDSON, Peter, C. et al.; Pfizer Inc., 235 East 42nd Street, New York, NY 10017 (US).  <b>(81) Designated States:</b> AU, CA, JP, KR, NO, RU, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published <i>With international search report.</i>
<b>(54) Title:</b> IONIC COMPLEXES OF IONIZABLE EMULSIFIERS WITH IONIZABLE POLYPEPTIDES AND/OR ION- IZABLE HYDROCOLLOIDS  <b>(57) Abstract</b>  The invention relates to ionic complexes of ionizable emulsifiers with ionizable polypeptides and/or ionizable hydrocol- loids. The complexes are useful as fat substitutes, food opacifiers, foam stabilizers and flavor modifiers. They are further useful as stiffeners for oils and oil-water emulsions allowing the use of normally liquid unsaturated oils in place of saturated fats in food compositions such as shortenings and spreads.		

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5                    IONIC COMPLEXES OF IONIZABLE EMULSIFIERS WITH  
                     IONIZABLE POLYPEPTIDES AND/OR IONIZABLE HYDROCOLLOIDS

Background of the Invention

                     The present invention relates to ionic complexes comprising emulsifiers. More particularly, it refers to ionic complexes of ionizable emulsifiers with ionizable  
10 polypeptides and/or ionizable hydrocolloids.

                     Our society, with its preoccupation with health and especially excess body weight, has generated a large demand for foods consonant with this outlook. Foremost in this regard are foods with reduced levels of calories and fat which retain the desirable organoleptic properties of traditional calorie- and fat-rich foods.

15                    Fat performs a number of functions in food. It is a major contributor to the mouthfeel and texture of many foods. Additionally, fat is largely responsible for the opacity and sheen of foods such as sour cream, mayonnaise and ice cream. In foods such as butter and margarine, the crystalline nature of fats provides the structure necessary for the product. In baked goods, fat is important for the desirable texture of  
20 many products and prevention of staling.

                     However, consumption of high levels of fat is not consistent with desirable goals of avoiding excess body weight and maintenance of optimum cardiovascular function. The average percentage of calories from fat in the American diet has been estimated as 41-42% (U.S. Department of Agriculture, Nationwide Food Consumption Survey 1977  
25 -78. Report No. 1-2. Consumer Nutrition Division, Human Nutrition Information Service, Hyattsville, MD (1984)). In sharp contrast to this, public health officials have recommended limiting consumption of fat to a level which contributes 30% of the calories in the diet. (U.S. Department of Agriculture/U.S. Department of Health and Human Services, Nutrition and Your Health: Dietary Guidelines for Americans, 2nd ed.  
30 Home and Garden Bulletin No. 232, U.S. Government Printing Office, Washington, D.C. (1985)).

                     In addition to the overall fat level in the diet, the specific nature of the fatty acids comprising dietary fat has been the subject of much recent interest. (G. J. Nelson, ed., Health Effects of Dietary Fatty Acids, American Oil Chemists' Society, Champaign, Ill.  
35 (1991)). Saturated fatty acids have been widely implicated as raising plasma total cholesterol levels and unfavorably shifting the distribution of plasma lipoproteins from the desirable high density lipoproteins (HDL's) to the low density lipoproteins (LDL's) implicated in cardiovascular disease. The C<sub>12</sub> (lauric), C<sub>14</sub> (myristic) and C<sub>16</sub> (palmitic)

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fatty acids have been implicated as the primary cholesterol-raising components of dietary fat, while stearic acid ( $C_{18}$ ) has been demonstrated not to have this undesirable effect. (S. M. Grundy, "Which Saturated Fatty Acids Raise Plasma Cholesterol Levels?" *Ibid* pp. 83-93.) Most recently, trans-unsaturated fatty acids, formed during the hydrogenation of vegetable oils, have been shown to have the same undesirable effects on blood lipids as do the  $C_{12}$ - $C_{16}$  fatty acids. (R. P. Mensink and M. B. Katan, *New England Journal of Medicine*, 323, pp. 439-445 (1990)).

In many foods, it is desirable for textural, structural and organoleptic effects to use fats which are largely crystalline at normal temperatures. Thus, butter owes its structure to the high degree of saturated fatty acids contained in butterfat. Margarine is prepared from hydrogenated vegetable oil, in which saturated and trans-unsaturated fatty acids are present in large amounts and contribute crystallinity. Both butter and margarine are water-in-oil emulsions which owe their stability to the crystalline nature of the fat. In reduced-fat spreads designed to be more healthful alternatives to butter and margarine, the stabilizing influence of fats containing saturated and trans-unsaturated fatty acids becomes more important to the product's structure as more and more water is incorporated to reduce fat levels.

Baked goods owe their pleasing mouthfeel and texture to the use of shortening, which significantly modifies the gluten structure of the dough. Shortening consists of hydrogenated vegetable oil, animal fat (such as lard or suet) or the so-called tropical oils (palm oil, palm kernel oil and coconut oil) which contain high levels of saturated fatty acids.

In both of the above cases a major contribution to a more healthy diet could be made if natural vegetable oils could be substituted for hard and hydrogenated fats.

Many low-fat foods suffer from a lack of opacity. This is particularly true of dairy products such as sour cream and mayonnaise. In these foods, the opacity and sheen typical of the full-fat product is due to tiny globules of fat in the food emulsion. Consumer acceptance of low-fat versions of these products could be increased, with heightened health benefits, by increasing opacity and sheen.

United States Patent No. 4,411,926 describes the preparation of a protein stabilizer for frozen foamed emulsions which comprises co-drying an aqueous dispersion comprising a protein, an ionizable or non-ionizable emulsifier and a sugar, the pH of the emulsion having been adjusted to between 6.0 and 9.0 by addition of a base.

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United States Patent No. 4,615,900 describes the use of the protein stabilizer of United States Patent No. 4,411,926 to improve the flavor impact and mouthfeel of beverages.

European Patent Application No. 238,330 refers to modified emulsifiers, useful  
5 in the preparation of food and beverage emulsions formed from oppositely charged emulsifiers and hydrocolloids and a stabilizer comprising a network-forming component.

T. Joensson describes the use of pectin/alginate emulsifier combinations in cereal based food. (Research Disclosure 28642, February, 1988).

L. Mars describes his study of the extent and mechanism of the interaction of  
10 the anionic hydrocolloid xanthan gum with a polyoxyethylene nonionizable surfactant, an anionic surfactant, sodium dodecylsulfate (which required added divalent cations), and the cationic surfactant cetyltrimethylammonium bromide. [Abstract of Dissertation, in Dissertation Abstracts International, 51, 5339-40B (1991)].

Japanese Patent Application 2109942 describes a gel contained in meat or fish  
15 processed food, obtained by heat treatment or treatment at a low temperature of an aqueous mixture of emulsifier, soybean protein and water.

European Patent Application No. 440,561 describes a means of purifying protein by precipitation with fatty acids.

Japanese Patent Applications Nos. 63071133 and 63071134 describe bread  
20 improving agents containing natural gums and glyceride fatty acid esters.

#### Summary of the Invention

The present invention provides a new class of ionic complexes of ionizable emulsifiers with ionizable polypeptides and/or ionizable hydrocolloids and the process of employing these complexes in food compositions. These complexes function as fat  
25 mimetics, oil stiffeners, emulsion stiffeners, opacification agents, foam stabilizers, flavor modifiers, and emulsifiers.

An ionizable substance is one which contains polar functional groups which can become charged under conditions known to the art. For instance, ionizable emulsifiers include those containing carboxylic acid groups which upon dissolution or treatment  
30 with base form carboxylate ions.

In accordance with a first embodiment of the invention, there is provided a composition comprising an ionic complex formed from at least one ionizable emulsifier and one or more substances selected from the group consisting of ionizable polypeptides and ionizable hydrocolloids, with the proviso that if the charges on said

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emulsifier, polypeptide and hydrocolloid are of the same sign, said complex is formed in the presence of a cross-linking agent.

Unless otherwise indicated, all references to ionizable emulsifiers, ionizable polypeptides, ionizable hydrocolloids and cross-linking agents throughout this application are meant to include their salts.

According to a preferred modification of the first embodiment said emulsifier, polypeptide, hydrocolloid and cross-linking agent are edible.

A preferred aspect of the first embodiment is one wherein said polypeptide is a protein or protein hydrolyzate.

10 In a preferred aspect of the first embodiment the complex is formed from said emulsifier, polypeptide and hydrocolloid.

In another preferred aspect of the first embodiment the complex is formed from said emulsifier and polypeptide in the absence of said hydrocolloid.

Another preferred aspect of the above embodiment provides for a complex  
15 formed from said emulsifier and hydrocolloid in the absence of said polypeptide.

Yet another aspect of the embodiment is one wherein the charges on said emulsifier, polypeptide and/or hydrocolloid are of the same sign and said complex is formed in the presence of a cross-linking agent.

According to a second embodiment of the invention there is provided a  
20 composition of the first embodiment, wherein said complex is prepared by

- a) admixing said emulsifier and an aqueous solution of said polypeptide and/or hydrocolloid and said crosslinking agent, if present, and
- b) heating and stirring the resultant mixture until any precipitate formed in a) disperses in the aqueous medium to form a dispersion.

25 In another aspect of the second embodiment the process further comprises treating the above-indicated dispersion with a pH adjusting composition until the viscosity and opacity of the mixture is raised to a desired level.

A third embodiment of the invention provides for a foodstuff comprising a composition comprising an ionic complex formed from at least one ionizable emulsifier and one or more substances selected from the group consisting of ionizable polypeptides and ionizable hydrocolloids, with the proviso that if the charges on said  
30 emulsifier, polypeptide and hydrocolloid are of the same sign, said complex is formed in the presence of a cross-linking agent.

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Another aspect of the above embodiment provides foodstuffs comprising said complex, said foodstuff selected from the group consisting of spreads, margarines, shortenings, frozen desserts, salad dressings, dips for crackers, dips for chips, dips for vegetables, confections having normally present triglycerides, whipped toppings, frostings, fillings for cakes, fillings for cookies, whipped desserts, gelled desserts, puddings, beverages, soups, and baked goods.

A fourth embodiment of the invention provides a process for preparing a composition comprising an ionic complex formed from at least one ionizable emulsifier, and one or more substances selected from the group consisting of ionizable polypeptides and ionizable hydrocolloids, with the proviso that if the charges on said emulsifier, polypeptide and hydrocolloid are of the same sign, said complex is formed in the presence of a cross-linking agent, wherein said process comprises the steps of

- a) admixing said emulsifier, an aqueous solution of said polypeptide and/or hydrocolloid, and said crosslinking agent, if present;
- and b) heating and stirring said mixture until any precipitate formed therein disperses in the aqueous medium.

In another aspect of the above embodiment the process further comprises treating the above-indicated dispersion with a pH adjusting composition until the viscosity and opacity of the mixture is raised to a desired level.

According to a fifth embodiment of the invention there is provided a method for reducing the fat content of a food containing an edible oil or fat comprising replacing at least a portion of the normally present edible oil or fat with a composition comprising an ionic complex formed from at least one ionizable emulsifier and one or more substances selected from the group consisting of ionizable polypeptides and ionizable hydrocolloids, with the proviso that if the charges on said emulsifier, polypeptide and hydrocolloid are of the same sign, said complex is formed in the presence of a cross-linking agent.

Another embodiment of the invention provides a method of using an ionic complex as described with respect to the first embodiment to increase the viscosity of oils.

Yet another embodiment of the present invention provides a method of using an ionic complex as described with respect to the first embodiment to increase the viscosity of emulsions.

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Another embodiment of the invention provides a method of using an ionic complex as described with respect to the first embodiment to increase the opacity of low fat emulsions.

Yet another embodiment of the invention provides a method for using an ionic  
5 complex as described with respect to the first embodiment as a fat substitute.

#### Detailed Description of the Invention

The instant invention is directed to a composition comprising an ionic complex formed from at least one ionizable emulsifier, and one or more substances selected from the group consisting of ionizable polypeptides and ionizable hydrocolloids, with  
10 the proviso that if the charges on said emulsifier, polypeptide and hydrocolloid are of the same sign said complex is formed in the presence of a cross-linking agent.

A preferred composition is one wherein the complex is formed from at least one ionizable emulsifier, at least one ionizable polypeptide and at least one ionizable hydrocolloid.

15 Another preferred composition is one wherein said complex is formed from said emulsifier and polypeptide in the absence of an ionizable hydrocolloid.

Yet another preferred composition is one wherein said complex is formed from said emulsifier and hydrocolloid in the absence of an ionizable polypeptide.

In a most preferred composition said ionizable polypeptide is a protein.

20 Emulsifiers for use in the practice of the invention are selected from the group consisting of ionizable group containing esters of fatty acids with polyhydroxy compounds, ionizable group containing esters of fatty alcohols with acids selected from the group consisting of polycarboxylic, poly(sulfato), poly(sulfonato), poly(phosphato) and poly(phosphonato) acids, lecithin and derivatives thereof; fatty acids; and  
25 combinations thereof.

The preferred polypeptides which may be used in the practice of the invention are proteins selected from the group consisting of milk proteins, animal proteins, vegetable proteins and combinations thereof.

Non-limiting examples of preferred proteins are casein, whey protein  
30 concentrate, sweet dairy whey, gelatin and derivatives (e.g., gelatin hydrolyzates and succinylated gelatin).

Non-limiting examples of hydrocolloids useful in the practice of the invention include carrageenan, alginic acid, agar, gum arabic, gum tragacanth, xanthan gum,



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gellan gum, furcellaran, carboxymethylcellulose, pectin, modified food starches and chitosan.

Cross-linking agents useful in the practice of the invention include polyvalent cations, polyvalent anions; and precursors thereof. The choice between polyvalent  
5 cations and polyvalent anions will be determined by the sign of the charges on said emulsifier, polypeptide and/or hydrocolloid.

Polyvalent anions useful in the practice of the invention are illustrated by  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , borates, poly(sulfonato) organic compounds, poly(sulfato) organic compounds, poly(phosphonato) organic compounds, poly(phosphato) organic  
10 compounds, poly(carboxyl) compounds; precursors thereof; and combinations thereof wherein the polyvalent cations are exemplified by polyvalent cations of elements of groups II and III of the Periodic Table, transition metals, polyammonium compounds; and combinations thereof.

$\text{HSO}_4^-$  and  $\text{H}_2\text{PO}_4^-$  are examples of precursors for polyvalent anions.

15 Preferred polyvalent cations are selected from Calcium (Ca), Chromium (Cr), Iron (Fe), Aluminum (Al), Titanium (Ti) and Vanadium (V); and combinations thereof.

It will be appreciated by those skilled in the art to which this invention applies that the choice amongst members of each of the above listed groups will generally be made in accordance with the specific application for which the composition is to be  
20 used.

For instance, if the application is to be an oral one, the polypeptide or polyvalent cation used would be ones which are approved as food additives. In other instances, non food additive approved components could be used in preparing compositions according to the instant invention for non-oral use such as in ointments.

25 In a preferred aspect of the invention, the complex further comprises a pH adjusting agent which will effect increases in the viscosity and/or opacity of aqueous dispersions of the composition.

A preferred complex of the above composition comprises from about 0.1 to about 99.98 % of said emulsifier, from about 0.01 to about 99.5 % of said polypeptide  
30 and from about 0.01 to about 40 % of said hydrocolloid.

More preferably the above complex comprises from about 5 to about 50 % of said emulsifier, from about 50 to about 95 % of said polypeptide and from about 0.1 to about 2.5 % of said hydrocolloid.

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Another preferred complex of the above composition comprises from about 0.1 to about 90 % of said emulsifier and from about 10 to about 99.9 % of said polypeptide and no ionizable hydrocolloids.

More preferably the complex comprises from about 5 to about 50 % of said  
5 emulsifier and from about 50 to about 95 % of said polypeptide.

Yet another preferred complex of the above composition comprises from about 60 to about 99.99 % of said emulsifier and from about 0.01 to about 40 % of said hydrocolloid and no polypeptide.

More preferably said complex comprises from about 95 to about 99.9 % of said  
10 emulsifier and from about 0.1 to about 5 % of said hydrocolloid.

Specific proportions of the various components will be chosen by the user in accordance with the requirements of his application.

In another modification of the invention the composition comprises an aqueous dispersion of one of the above-indicated complexes.

15 According to another embodiment of the invention there is a provided a composition comprising an ionic complex as described with respect to the first embodiment wherein said complex is prepared by

a) admixing said emulsifier and an aqueous solution of said polypeptide and/or hydrocolloid or salts thereof and said crosslinking composition, if present,  
20 and b) heating and stirring the above mixture until any precipitate formed in step a) disperses in the aqueous medium to form a dispersion.

In another aspect of the above embodiment the process further comprises treating the above-indicated dispersion with a pH adjusting composition until the viscosity and opacity of the mixture is raised to a desired level.

25 In a preferred aspect of the above embodiment the dispersion is dehydrated. Dehydration may be effected by any means known to the art including freeze-drying, rotary evaporation, high vacuum drying and spray drying.

The composition of the invention may be used in its dehydrated form or dispersed in an aqueous medium. The aqueous dispersion may be the above  
30 indicated dispersion formed during preparation of the composition or it may be a reconstituted dispersion formed from the dehydrated composition.

The emulsifiers, polypeptides, hydrocolloids and cross-linking agents useful in the practice of this aspect of the invention have been described above with respect to the first embodiment.

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A third embodiment of the invention provides a foodstuff comprising the above-indicated ionic complexes of the invention.

The emulsifiers, polypeptides, hydrocolloids and cross-linking agents useful in the practice of the foodstuff embodiment are components approved for food use. The user will select specific components, in accordance with the desired application, from amongst those which are Generally Recognized as Safe (GRAS) or approved as food additives or ingredients.

In a preferred aspect of the above embodiment the foodstuff will also comprise at least one additive selected from the group consisting of edible fats or oils, fat mimetics, gel-forming compositions, flavorants, colorants, sweeteners, fat extenders and salts.

A fourth embodiment of the invention comprises a process, for preparing a composition comprising an ionic complex as described with respect to the first embodiment, which comprises the steps of

- a) admixing said emulsifier, an aqueous solution of said polypeptide and/or hydrocolloid, or salts thereof and said crosslinking agent, if present;
- and b) heating and stirring the resultant mixture until any precipitate formed therein disperses in the aqueous medium.

In the practice of this embodiment of the invention, the emulsifier is added to an aqueous solution of the polypeptide and/or hydrocolloid and cross-linking agent, if present. A precipitate is formed. The resultant mixture is heated and stirred until the precipitate is dispersed in the aqueous medium to form a dispersion.

In a preferred aspect the above embodiment further comprises the process of dehydrating said dispersion. The dehydration step may be effected by any means known to the art including freeze-drying, rotational evaporation drying, vacuum drying and spray drying.

Another preferred aspect of this embodiment comprises the step of forming an aqueous dispersion of the above composition by redispersing the above-indicated dehydrated product in an aqueous dispersion.

In accordance with a fifth embodiment of the invention there is provided a method for reducing the fat content of a food containing an edible oil or fat comprising replacing at least a portion of the normally present edible oil or fat with a composition comprising any of the ionic complexes described above.

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Another preferred modification of the above embodiment comprises an aqueous dispersion medium.

In yet another aspect of the above embodiment said composition comprises at least one additive selected from the group consisting of edible oils and fats, fat  
5 mimetics, gel-forming compositions, acidic pH adjusting agents, flavorants, colorants, sweeteners, fat extending compositions, and salts.

Fat mimetics useful in the practice of the invention include polyol fatty acid esters, sugar fatty acid esters, polyglycerol fatty acid esters, fatty acid esters of epoxide-extended polyols, fatty acid/fatty alcohol carboxy/carboxylate esters,  
10 polysiloxanes, polyoxyalkylene fatty acid esters, fatty alcohol esters of polycarboxylic acids, malonic acid fatty alcohol diesters, alkyl malonic acid fatty alcohol diesters and dialkyl malonic acid fatty alcohol diesters; alkyl glycoside fatty acid polyesters, alpha-acylated fatty acid triglycerides, glycerol fatty alcohol diethers, monoglyceride fatty alcohol diethers, glycerol esters of alpha-branched carboxylic acids, diol lipid  
15 analogues, poly(vinyl alcohol) fatty acid esters, tris(hydroxymethyl)alkyl esters of fatty acids, dicarboxylate-extended fatty acid derivatives, cycloalkyldiol esters, primary amide esters, amide/ether/ester derivatives, complex linked esters, and triglycerides esterified at the 1- and 3-positions with saturated long chain fatty acids and at the 2-position with a short-chain acid.

20 The emulsifiers, polypeptides, hydrocolloids, cross-linking agents, pH adjusting agents and additives useful in the practice of this embodiment of the invention have been described above with respect to the other embodiments.

The compositions of the instant invention are useful as oil stiffeners, e.g., in dough additives to mimic shortening behavior with vegetable oil, in cheese analogs  
25 employing vegetable oils rather than milkfat and in spread compositions employing polyunsaturated vegetable oils rather than saturated or partially hydrogenated fats; as texturizers, e.g. in low-fat meat products, candies such as nougats and caramels, cheese analogs, peanut butter, creamy salad dressings; as opacifiers in, for instance, mayonnaise, sour cream, dairy sauces, soups, instant (dry mix) sauces and beverages  
30 (as a replacement for brominated vegetable oil); and as foam stabilizers in, e.g., whipped toppings, frozen dairy deserts, puddings and mousses; as flavor modifiers, e.g., in softening the impact of sharp flavor components (such as aldehydes) in lower-fat foods; as drug delivery vehicles; and as a means of improving stability and

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acceptability of  $\omega$ -3 and  $\omega$ -6 fatty acids in foods by complexation of the acids with, e.g., polypeptides.

The invention having been described in general terms, reference is now made to specific examples. It is to be understood that these examples are not meant to limit  
5 the present invention, the scope of which is determined by the appended claims.

#### EXAMPLE 1

##### COMPLEX OF HYDROLYZED GELATIN WITH STEARIC ACID

With stirring, 40.0 grams of Hormel Polypro 5000 hydrolyzed gelatin was added to 600 grams of deionized water. After the gelatin had dissolved, 100.0 grams of  
10 Henkel-Emersol 6332 60/40 stearic/palmitic acid was added and the mixture was slowly heated with continued stirring. When the temperature reached approximately 55°C, a waxy precipitate formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 4.5 to 6.8 with 50% sodium hydroxide solution. During pH adjustment, the mixture rapidly  
15 increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room temperature, then refrigerated. The chilled product had the appearance, odor, and texture of tallow.

#### EXAMPLE 2

##### COMPLEX OF HYDROLYZED GELATIN WITH DIACETYLTARTARIC ACID

20

##### ESTERS OF MONOGLYCERIDES

With stirring, 40.0 grams of Hormel Polypro 5000 hydrolyzed gelatin was added to 600 grams of deionized water. After the gelatin had dissolved, 100.0 grams of Grindsted Panodan 150 (monoglycerides and diacetyltartaric acid esters of monoglycerides) was added and the mixture was slowly heated with continued stirring.  
25 When the temperature reached approximately 45°C, a waxy precipitate formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 2.8 to 6.8 with 50% sodium hydroxide solution. During pH adjustment, the mixture rapidly increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room  
30 temperature, then refrigerated. The chilled product had the appearance and texture of a soft fat with a slight cereal-like odor.

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EXAMPLE 3COMPLEX OF CALCIUM-CROSSLINKED CARRAGEENAN WITH STEARIC ACID

In a Waring blender running at approximately 50% of full power, 0.8 gram of FMC Gelcarin GP812 carrageenan was added to 100 grams of deionized water, and blending was continued for about 3 minutes until the carrageenan had dissolved. With stirring, the resulting solution was added to 500 grams of deionized water. With continued stirring, 1.7 grams of calcium lactate and 100.0 grams of Henkel-Emersol 6332 60/40 stearic/palmitic acid was added, and the mixture was slowly heated. When the temperature reached approximately 55°C, a waxy precipitate formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 5.0 to 6.8 with 50% sodium hydroxide solution. During pH adjustment, the mixture rapidly increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room temperature, then refrigerated. The chilled product was white and brittle, with a tallow-like odor.

EXAMPLE 4COMPLEX OF WHEY PROTEIN WITH STEARIC ACID

With stirring, 40.0 grams of BiPro 95 95% whey protein concentrate was added to 600 grams of deionized water. After the protein had dissolved, 100.0 grams of Henkel-Emersol 6332 60/40 stearic/palmitic acid was added and the mixture was slowly heated with continued stirring. When the temperature reached approximately 55°C, a waxy precipitate formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 4.5 to 6.8 with 50% sodium hydroxide solution. During pH adjustment, the mixture rapidly increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room temperature, then refrigerated. The chilled product had the appearance, odor, and texture of a soft fat.

EXAMPLE 5COMPLEX OF WHEY PROTEIN WITH DIACETYLTARTARIC ACIDESTERS OF MONOGLYCERIDES

With stirring, 40.0 grams of BiPro 95 95% whey protein concentrate was added to 600 grams of deionized water. After the protein had dissolved, 100.0 grams of Grindsted Panodan 150 (diacetyltartaric acid esters of monoglycerides with added monoglycerides) was added and the mixture was slowly heated with continued stirring.

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When the temperature reached approximately 55°C, a waxy precipitate formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 2.8 to 6.8 with 50% sodium hydroxide solution. During pH adjustment, the mixture rapidly increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room temperature, then refrigerated. The chilled product had the appearance and texture of a tallow with a slight cereal-like odor.

#### EXAMPLE 6

##### 10                    COMPLEX OF MILK PROTEIN WITH STEARIC ACID

With stirring, 40.0 grams of Ecco Code 100 milk protein (Erie Foods) was added to 600 grams of deionized water. After the protein had dissolved, 100.0 grams of Henkel-Emersol 6332 60/40 stearic/palmitic acid was added and the mixture was slowly heated with continued stirring. When the temperature reached approximately 55°C, a waxy precipitate formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 4.5 to 6.8 with 50% sodium hydroxide solution. During pH adjustment, the mixture rapidly increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room temperature, then refrigerated. The chilled product had the appearance, odor, and mixture of tallow.

#### EXAMPLE 7

##### COMPLEX OF MILK PROTEIN WITH DIACETYLTARTARIC ACID ESTERS OF MONOGLYCERIDES

With stirring, 40.0 grams of Ecco Code 100 milk protein (Erie Foods) was added to 600 grams of deionized water. After the protein had dissolved, 100.0 grams of Grindsted Panodan 150 (monoglycerides) was added and the mixture was slowly heated with continued stirring. When the temperature reached approximately 55°C, a waxy precipitate formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 2.8 to 6.8 with 50% sodium hydroxide solution. During pH adjustment, the mixture rapidly increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room temperature, then refrigerated. The chilled product had the appearance, odor, and texture of soft fat.

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EXAMPLE 8WHEY PROTEIN - EMULSIFIER COMPLEX IN AGAR-STARCH MATRIX

With stirring, 108.0 grams of BiPro 95 95% whey protein concentrate was added to 1622 grams of deionized water. After the protein had dissolved, 270.2 grams of

5 Grindsted Panodan 150 (diacetyltartaric acid esters of monoglycerides with added monoglycerides) was added and the mixture was slowly heated with continued stirring. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 2.8 to 6.8 with 50% sodium hydroxide solution. In a separate vessel, a mixture of 2894 grams of water, 76.5 grams of MiraThik 468 modified food starch

10 (Staley Corp.) and 30.0 grams of agar was heated to 90°C with stirring. When the solids had dissolved, the still-hot (70°C) protein-emulsifier complex was added with continued stirring. The mixture was pasteurized by stirring at 70-75°C for 30 minutes, then allowed to cool. At 50°C, 5.85 grams of potassium sorbate was added. At 35°C, the pH was adjusted to 4.5 with 75% phosphoric acid. The resulting emulsion was

15 passed through a two-stage homogenized at 2500 pounds per square inch followed by 500 pounds per square inch, then refrigerated.

EXAMPLE 9HYDROLYZED GELATIN - STEARIC ACID COMPLEX IN AGAR-STARCH MATRIX

With stirring, 108.0 grams of Hormel Polypro 5000 hydrolyzed gelatin was added

20 to 1622 grams of deionized water. After the gelatin had dissolved, 270.2 grams of Henkel-Emersol 6332 60/40 stearic/palmitic acid was added and the mixture was slowly heated with continued stirring. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 4.5 to 6.8 with 50% sodium hydroxide solution. In a separate vessel, a mixture of 2894 grams of water, 76.5 grams of MiraThik 468

25 modified food starch (Staley Corp.) and 30.0 grams of agar was heated to 90°C with stirring. When the solids had dissolved, the still-hot (70°C) gelatin - stearic acid complex was added with continued stirring. The mixture was pasteurized by stirring at 70-75°C for 30 minutes, then allowed to cool. At 50°C, 5.85 grams of potassium sorbate was added. At 35°C, the pH was adjusted to 4.5 with 75% phosphoric acid.

30 The resulting dispersion was passed through a two-stage homogenized at 2500 pounds per square inch followed by 500 pounds per square inch, then refrigerated.



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EXAMPLE 10COMPLEX OF WHEY PROTEIN WITH SODIUM STEAROYL LACTYLATE

With stirring, 20.0 grams of BiPro 95 95% whey protein concentrate was added to 300 grams of deionized water. After the protein had dissolved, 50.0 grams

5 Grindsted Artodan SP55K sodium stearoyl lactylate was added and the mixture was slowly heated with continued stirring. When the temperature reached approximately 55°C, a waxy precipitate formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 4.5 to 6.8 with 50% sodium hydroxide solution. During pH adjustment,

10 the mixture rapidly increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room temperature, then refrigerated. The chilled product had the appearance, odor, and texture of hard fat.

EXAMPLE 11COMPLEX OF WHEY PROTEIN WITH FATTY ACIDS

15 With stirring, 20.0 grams of BiPro 95 95% whey protein concentrate was added to 300 grams of deionized water. After the protein had dissolved, 25.0 grams of Henkel-Emersol 6332 60/40 stearic/palmitic acid and 25.0 grams of high oleic fatty acids from sunflower oil were added and the mixture was slowly heated with continued stirring. When the temperature reached approximately 55°C, a waxy precipitate

20 formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 4.5 to 6.8 with 50% sodium hydroxide solution. During pH adjustment, the mixture rapidly increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room temperature, then refrigerated. The chilled product had the appearance and odor of

25 soft fat.

EXAMPLE 12COMPLEX OF CALCIUM-CROSSLINKED SODIUM ALGINATEWITH DIACETYL TARTARIC ACID ESTERS OF MONOGLYCERIDES

In a Waring blender running at approximately 50% of full power, 0.8 gram kelco

30 Kelton HV sodium alginate was added to 100 grams of deionized water, and blending was continued for about 3 minutes until the alginate had dissolved. With stirring, the resulting solution was added to 500 grams of deionized water. With continued stirring, 1.7 grams of calcium lactate and 100.0 grams of Grindsted Panodan 150 (monoglycerides and diacetyl tartaric acid esters of monoglycerides) was added, and

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the mixture was slowly heated. When the temperature reached approximately 55°C, a waxy precipitate formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 2.8 to 6.8 with 50% sodium hydroxide solution. During pH adjustment, the mixture rapidly increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room temperature, then refrigerated. The chilled product was white and brittle, with a tallow-like odor.

#### EXAMPLE 13

##### FREEZE-DRIED HYDROLYZED GELATIN - STEARIC ACID COMPLEX

10 A 250-gram portion of a hydrolyzed gelatin - stearic acid complex prepared according to Example 1 was freeze-dried to a light, friable white solid.

#### EXAMPLE 14

##### FREEZE-DRIED MILK PROTEIN - STEARIC ACID COMPLEX

15 A 250-gram portion of a milk protein - stearic acid complex prepared according to Example 6 was freeze-dried to a light, friable white solid.

#### EXAMPLE 15

##### ROTARY-EVAPORATED HYDROLYZED GELATIN - STEARIC ACID COMPLEX

20 A 100-gram portion of a hydrolyzed gelatin - stearic acid complex prepared according to Example 1 was concentrated by rotary evaporation at approximately 70°C, then dried under high vacuum (<0.1 mm Hg) to a cream-colored solid containing less than 1 percent water.

#### EXAMPLE 16

##### COMPLEX OF CALCIUM-CROSSLINKED CARRAGEENAN

##### WITH DIACETYL TARTARIC ACID ESTERS OF MONOGLYCERIDES

25 In a Waring blender running at approximately 50% of full power, 0.8 gram of FMC Gelcarin GP812 carrageenan was added to 100 grams of deionized water, and blending was continued for about 3 minutes until the carrageenan had dissolved. With stirring, the resulting solution was added to 500 grams of deionized water. With continued stirring, 1.7 grams of calcium lactate and 100.0 grams of Grindsted Panodan  
30 150 (monoglycerides and diacetyltartaric acid esters of monoglycerides) was added, and the mixture was slowly heated. When the temperature reached approximately 55°C, a waxy precipitate formed, then dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, the pH was adjusted from approximately 2.8 to 6.8 with 50% sodium hydroxide solution. During pH adjustment, the mixture

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rapidly increased in opacity and viscosity. The hot mixture was transferred to a jar, allowed to cool to room temperature, then refrigerated. The chilled product was white and brittle, with a slightly acidic odor.

#### EXAMPLE 17

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#### FREEZE-DRIED COMPLEX OF WHEY PROTEIN WITH DIACETYLTARTARIC ACID ESTERS OF MONOGLYCERIDES

A complex of whey protein with diacetyltartaric acid esters of monoglycerides, prepared accordingly to Example 5, was freeze-dried to a light, friable white solid.

#### EXAMPLE 18

10

#### FREEZE-DRIED CHITOSAN - STEARIC ACID COMPLEX

With stirring, 1.1 gram of Sigma C-092 chitosan and 142 grams of Henkel-Emersol 6353 stearic acid (greater than 90% stearic acid) was added, and stirring was continued for 30 minutes. With continued stirring, the mixture was slowly heated. When the temperature reached approximately 65°C, a waxy precipitate formed, then  
15 dispersed upon continued stirring and heating. When the temperature of the mixture reached 75°C, stirring was continued for 30 minutes to effect pasteurization. The pH was then slowly raised from approximately 4.5 to 6.8 by addition of 50% sodium hydroxide solution. During pH adjustment, the mixture rapidly increased in opacity and viscosity. The hot mixture was transferred to bottles, frozen, and freeze-dried to a white  
20 powder. A portion of the powder was rehydrated at 10% in water at 75°C, then cooled to room temperature to a white ointment-like material with the appearance of soft fat.

#### EXAMPLE 19

#### FREEZE-DRIED COMPLEX OF CALCIUM-CROSSLINKED SODIUM ALGINATE WITH DIACETYLTARTARIC ACID ESTERS OF MONOGLYCERIDES

25

A complex of calcium-crosslinked sodium alginate with diacetyltartaric acid esters of monoglycerides, prepared according to Example 12, was freeze-dried to a light, friable white solid.

#### EXAMPLE 20

#### FREEZE-DRIED WHEY PROTEIN - STEARIC ACID COMPLEX

30

A whey protein - stearic acid complex prepared according to Example 4 was freeze-dried to a light, friable white solid.

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EXAMPLE 21COMPLEX OF SODIUM CASEINATE WITH DIACETYLTARTARIC ACID ESTERS  
OF MONOGLYCERIDES AND STEARIC ACID

With stirring, 200.0 grams of Ecco Code 400 sodium caseinate (Erie Foods) was  
5 added to 3000 grams of deionized water. After the protein had dissolved, 250.0 grams  
of Grindsted Panodan 150 (diacetyltartaric acid esters of monoglycerides with added  
monoglycerides) and 250.0 grams of Henkel Emersol 6353 (greater than 90% stearic  
acid) were added and the mixture was slowly heated with continued stirring. When the  
temperature reached approximately 55°C, a waxy precipitate formed, then dispersed  
10 upon continued stirring and heating. When the temperature of the mixture reached  
75°C, the pH was adjusted from approximately 4.2 to 6.8 by addition of 50% sodium  
hydroxide solution. During pH adjustment, the mixture rapidly increased in opacity and  
viscosity. The hot mixture had the appearance of opaque molten fat.

EXAMPLE 22

15 SPRAY-DRIED COMPLEX OF SODIUM CASEINATE WITH DIACETYLTARTARIC  
ACID ESTERS OF MONOGLYCERIDES AND STEARIC ACID

The product of Example 21 was spray dried to a free-flowing white powder.

EXAMPLE 23REDUCED FAT SPREAD

20 To a Waring® blender containing 150 grams of Puritan canola oil which had  
been heated to 40°C were added 150 grams of stearic acid - hydrolyzed gelatin  
complex prepared according to Example 1, 1.0 milliliter of Firmenich 57.752 artificial  
butter flavor, 4.5 grams of salt, 35 milligrams of Biocon WS7 turmeric powder, and 15  
milligrams of ITC WS-50-012577-00 annatto food color. The mixture was blended for  
25 3 minutes at 75% power, during which the sides of the blender jar were cleared  
frequently with a rubber spatula. The resulting mixture was passed through a hand  
homogenizer. The resulting spread was physically and organoleptically equivalent to  
a commercial spread containing 52% partially hydrogenated soybean and cottonseed  
oils.

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EXAMPLE 24FROSTING

	<u>Ingredients</u>	<u>Weight Percent</u>
	Protein-emulsifier complex prepared	
5	according to Example 4	20.30
	10x Powdered Sugar	71.60
	Globe 1132 corn syrup	3.00
	M100 maltodextrin (Grain Processing Corp.)	3.25
	MiraThik 469 modified food starch (Staley Corp.)	1.00
10	Vanilla extract	0.75
	Vanillin	<u>0.10</u>
		100.00

The protein-emulsifier complex was stirred for 1 minute at high speed with a Sunbeam Mixmaster®, the remaining ingredients were added, and mixing was continued for 1 minute. The resulting fat-free frosting was found to be organoleptically equivalent to a control containing 20.3% fat.

EXAMPLE 25FROZEN DESSERT

	<u>Ingredients</u>	<u>Weight Percent</u>
20	Protein-emulsifier complex in agar-starch matrix, prepared according to Example 8	2.00
	Skim milk	66.18
	Sugar	9.99
	M200 corn syrup solids (Grain Processing Corp.)	7.99
25	Polydextrose (Pfizer Inc Litesse)	5.19
	Nonfat milk solids	4.10
	M150 maltodextrin (Grain Processing Corp.)	4.00
	NFB emulsifier (Gold Star)	0.24
	Vanilla	0.18
30	2.5% solution of 1X annatto color (Pfizer Inc.)	<u>0.14</u>
		100.00

The skim milk was preheated to 38°C and transferred to a blender. With the blender running at 25 volts, the emulsifier was added and blending was continued for 2 minutes. The remaining ingredients except vanilla and annatto color were added and

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blending was continued for 2 minutes at 45 volts. The resulting mixture (2 kilograms) was pasteurized by heating in a 700W microwave oven until the temperature of the mixture reached 80°C, then continuing heating for one minute at full power. While hot, the mixture was homogenized at 2500 pounds per square inch then 500 pounds per square inch, cooled to 25°C in an ice bath, and refrigerated overnight. The vanilla and annatto colorant were added with stirring, and the resulting mixture was frozen with a small commercial ice cream freezer (Taylor Model 105) for approximately 7.5 minutes, hardened by exposure to dry ice temperature (-78°C) for 15 minutes, then transferred to a hardening freezer (-29°C) for storage. Paired comparison with a commercial fat-free frozen dessert by a 30-member sensory panel showed a statistically significant preference for the experimental frozen dessert at the 95% confidence level.

EXAMPLE 26REDUCED FAT MAYONNAISE

	<u>Ingredients</u>	<u>Weight Percent</u>
15	Protein-emulsifier complex in agar-starch matrix, prepared according to Example 8	19.69
	Water (A)	17.85
	Water (B)	20.67
	Water (C)	5.91
20	Vinegar	3.94
	Starch (National, Purity 4290A)	3.45
	Avicel RC591F microcrystalline cellulose (FMC)	1.97
	Xanthan gum	0.20
	M100 maltodextrin (Grain Processing Corp.)	5.91
25	Polydextrose (Pfizer Inc Litesse)	3.94
	M200 corn syrup solids (Grain Processing Corp.)	3.94
	Egg whites	5.91
	Lemon juice	2.46
	Salt	1.28
30	Sugar	0.98
	Mustard powder	0.44
	Onion powder	0.08
	Garlic powder	0.04
	White pepper	0.02

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	Sodium benzoate	0.10
	Potassium sorbate	0.10
	FD&C Yellow #5, 0.1% solution	0.28
	Beta carotene, 0.1% solution	<u>0.87</u>
5		100.00

The starch, vinegar, and water (B) were mixed and heated to 85°C for 10 minutes, and the mixture was allowed to cool. The xanthan gum was added to water (C) and allowed to prehydrate for about 5 minutes. In a Cuisinart® Food Processor, with stirring, the microcrystalline cellulose was added to water (A). Stirring was

10 continued for 10 minutes, the prehydrated xanthan gum mixture was added, stirring was continued for 3 minutes, all remaining ingredients except the starch mixture were added, stirring was continued for 3 minutes, the starch mixture was added, and stirring was continued for 3 minutes. The mixture was passed through a colloid mill at a setting of 8 microns and refrigerated. Paired comparison by a 30-member sensory

15 panel showed the experimental fat-free mayonnaise to be equivalent at the 95% confidence level to a fat-free mayonnaise made with a commercially available microparticulated protein as the fat substitute.

At 550 nm and a path length of 1 millimeter, the opacity of the experimental mayonnaise was 51%. A control made the same way but with water substituted for the

20 protein-emulsifier/agar-starch composition had an opacity of 43%.

EXAMPLE 27CHOCOLATE MOUSSE

	<u>Ingredients</u>	<u>Weight Percent</u>
25	Protein-emulsifier complex in agar-starch matrix, prepared according to Example 9	27.45
	Egg whites	20.86
	Semisweet chocolate (Bakers')	10.14
	Milk chocolate (Dove)	10.14
	Water (A)	12.35
30	Water (B)	3.53
	Egg yolks	10.78
	MiraGel 463 starch (Staley Corp.)	1.37
	MiraThik 468 starch (Staley Corp.)	1.37

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Nonfat milk solids	1.00
Vanilla extract	<u>1.00</u>
	100.00

In a double boiler, the chocolate was melted in water (B). The egg yolks were  
 5 beaten well, and with continued beating, the chocolate mixture was added gradually.  
 The resulting mixture was cooked for 90 seconds with continuous stirring. Heating was  
 discontinued and the vanilla was added with stirring. In a blender, with stirring, the  
 starches, nonfat milk solids, and protein-emulsifier complex were gradually added to  
 water (A) and blending was continued until the mixture was frothy. The resulting  
 10 mixture was folded into the egg yolk - chocolate mixture. The egg whites were whipped  
 until soft peaks formed, then folded into the egg yolk - chocolate mixture. The mixture  
 was homogenized by hand and refrigerated. The resulting low-fat chocolate mousse  
 was found to be acceptable when compared to a control containing 23.3% fat.

EXAMPLE 28

15

RANCH STYLE SALAD DRESSING

	<u>Ingredients</u>	<u>Weight Percent</u>
	Protein-emulsifier complex in agar-starch matrix, prepared according to Example 8	19.95
	Water (A)	13.64
20	Water (B)	20.95
	Water (C)	5.99
	Vinegar	3.99
	Starch (National, Purity 4290A)	3.49
	Avicel RC591F microcrystalline cellulose (FMC)	2.00
25	Xanthan gum	0.20
	M100 maltodextrin (Grain Processing Corp.)	3.99
	Polydextrose (Pfizer Inc Litesse)	3.99
	M200 corn syrup solids (Grain Processing Corp.)	2.99
	Egg whites	5.99
30	Lemon juice	2.49
	Salt	2.00
	Dijon mustard	3.99
	Worcestershire sauce	1.00
	Monosodium glutamate	0.30



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	Buttermilk Powder (Beatrice Foods San-a-milk 983)	2.00
	Onion Powder	0.15
	Garlic powder	0.10
	White pepper	0.03
5	Sodium benzoate	0.10
	Potassium sorbate	0.10
	FD&C Yellow #5, 0.1% solution	0.20
	Beta carotene, 0.1% solution	0.20
	Parsley	0.08
10	Dill	<u>0.11</u>
		100.00

The starch, vinegar, and water (B) were mixed and heated to 85°C for 10 minutes, and the mixture was allowed to cool. The xanthan gum was added to water (C) and allowed to prehydrate for about 5 minutes. In a Cuisinart® Food Processor, with stirring, the microcrystalline cellulose was added to water (A). Stirring was continued for 10 minutes, the prehydrated xanthan gum mixture was added, stirring was continued for 3 minutes, all remaining ingredients except the starch mixture were added, stirring was continued for 3 minutes, the starch mixture was added, and stirring was continued for 3 minutes. The mixture was passed through a colloid mill at a setting of 8 microns, the parsley and dill were added and folded in with a spatula, and the mixture was refrigerated. The resulting fat-free dressing was organoleptically equivalent to a control containing 7% soybean oil.

#### EXAMPLE 29

#### REDUCED FAT SPREAD

A mixture of 400 grams of Puritan canola oil, 4.8 grams of Grindsted Dimodan LSK monoglyceride emulsifier, 80 grams of freeze-dried hydrolyzed gelatin - stearic acid complex prepared according to Example 13, and low levels of  $\beta$ -carotene and Firmenich 57.752 artificial butter flavor was stirred at 80°C to soften and disperse the solids, then cooled in a ice bath. During cooling, the mixture was sheared with a Silverson® homogenizer-mixer equipped with an axial flow head and a fine screen, running at about 33% of full power, and a pasteurized solution of 8.0 grams of salt in 307 grams of water was added slowly. The mixer speed was increased as the emulsion stiffened. After all the salt solution had been added, the mixer speed was increased to about 75% of full power to invert the emulsion. Upon inversion, the viscosity of the emulsion

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dramatically increased. The inverted emulsion, at a temperature of about 25°C, was transferred to a Gelateria® scraped-wall ice cream maker, hardened by stirring until the temperature decreased to about 10°C, then transferred to containers for storage. The resulting spread was physically and organoleptically equivalent to a commercial spread containing 52% partially hydrogenated soybean and cottonseed oils.

EXAMPLE 30FROSTING

	<u>Ingredients</u>	<u>Weight Percent</u>
10	Polysaccharide-emulsifier complex prepared according to Example 3	20.30
	10x Powdered Sugar	71.60
	Globe 1132 corn syrup	3.00
	M100 maltodextrin (Grain Processing Corp.)	3.25
	MiraThik 469 modified food starch (Staley Corp.)	1.00
15	Vanilla extract	0.75
	Vanillin	<u>0.10</u>
		100.00

The polysaccharide-emulsifier complex was stirred for 1 minute at high speed with a Sunbeam Mixmaster®, the remaining ingredients were added, and mixing was continued for 1 minute. The resulting fat-free frosting was found to be organoleptically equivalent to a control containing 20.3% fat.

EXAMPLE 31UNFLAVORED WHIPPED TOPPING

	<u>Ingredients</u>	<u>Weight Percent</u>
25	Freeze-dried protein-emulsifier complex prepared according to Example 13	2.00
	Water	82.55
	Sugar	8.00
	M200 maltodextrin (Grain Processing Corp.)	6.00
30	Avicel RC591 microcrystalline cellulose (FMC)	0.50
	Avicel PH105 cellulose (FMC)	0.10
	Polysorbate 60 (Tween 60; ICI)	0.30
	Myverol 18.06 monoglycerides (Eastman Kodak)	0.15

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Hydroxypropyl cellulose (Aqualon-Klucel)	<u>0.40</u>
	100.00

The cellulose and microcrystalline cellulose were prehydrated in the water by stirring for 1 minute in a blender at approximately 40% of maximum power. The remaining ingredients were added, and blending was continued for 1 minute. The mixture was pasteurized by heating to 90°C for one minute, cooled to about 5°C, and refrigerated overnight. A 200-gram portion of the mixture was stirred in a Sunbeam MixMaster® for 1 minute at high speed, and for 1 minute at very high speed. The resulting unflavored whipped topping was judged to be physically and hedonically acceptable.

EXAMPLE 32  
SUGAR COOKIE

	<u>Ingredients</u>	<u>Weight Percent</u>
15	Freeze-dried protein-emulsifier complex prepared according to Example 17	2.7
	Water (A)	7.5
	Water (B)	16.9
	All-purpose flour	33.8
	10x Powdered Sugar	17.4
20	6x Granular Sugar	13.6
	Whole eggs	6.7
	Vanilla extract	0.5
	Cream of tartar	0.2
	Salt	0.4
25	Sodium bicarbonate	<u>0.3</u>
		100.0

The protein-emulsifier complex was hydrated in water (A) by vigorous mixing in a Waring® blender. The hydrated complex was added to the sugar, the mixture was stirred for 3 minutes at medium speed with a Sunbeam MixMaster®, the eggs, vanilla extract, and water (B) were added, and the mixing was continued for 1 minute. the remaining dry ingredients were premixed and added, and mixing was continued at low speed for 1 minute. The resulting batter was refrigerated for 3 hours. To make soft cookies, the resulting dough was formed into 13-gram balls which were flattened to discs about 5 centimeters in diameter on a Teflon-coated cookie sheet and baked for

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9 minutes at 375°C. To make snap cookies, the 13-gram balls of dough were flattened to discs about 6 centimeters in diameter and baked for 12 minutes at 375°F. the resulting cookies were found to be acceptable when compared to control cookies containing oil.

5

EXAMPLE 33  
SOUR CREAM SUBSTITUTE

	<u>Ingredients</u>	<u>Weight Percent</u>
	Freeze-dried alginate-emulsifier complex prepared according to Example 19	2.0
10	Water	65.7
	Sealtest no-fat cottage cheese	10.0
	Nonfat dry milk solids	6.0
	Polydextrose (Pfizer Inc Litesse)	4.5
	Modified food starch (National Starch UltraTex 4)	4.0
15	Corn syrup solids (Staley Star-Dri 42R)	2.5
	M150 maltodextrin (Grain Processing Corp.)	2.0
	Sour cream flavor (Haarman & Reimer R7365/261917)	1.0
	Sour cream flavor (Haarman & Reimer R7038/261062)	1.0
	Salt	0.5
20	Lactic acid (Johnson & Mathey 88% USP)	0.4
	Sodium citrate	0.2
	Xanthan gum	<u>0.2</u>
		100.0

The xanthan gum was prehydrated in the water by stirring for 2 minutes in a Waring® blender at approximately 50% of maximum power. The polydextrose, modified food starch, corn syrup solids, maltodextrin, alginate-emulsifier complex, and salt were added with thorough mixing after each addition, blender power was increased to approximately 80% of maximum, the cottage cheese was added, mixing was continued for 5 minutes, the lactic acid, sodium citrate, and flavors were added, mixing was continued for 2 minutes, and the mixture was transferred to a plastic tub and refrigerated. The resulting sour cream substitute was similar in texture, flavor, and appearance to 18% fat sour cream.

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EXAMPLE 34GELATION OF VEGETABLE OILWITH WHEY PROTEIN - STEARIC ACID COMPLEX

With stirring in a Waring® blender at low speed, 7.5 grams of freeze-dried whey protein - stearic acid complex prepared according to Example 20 was added to 42.5 grams of Wesson canola oil. The mixture was blended at medium speed for 2 minutes. A portion was transferred to a Searle type viscometer with programmable temperature controller, and apparent viscosity was monitored at a continuous shear rate of 132 sec<sup>-1</sup>. Initial viscosity at 25°C was 156 mPa•s. The sample was heated to 85°C, then cooled. During cooling, the sample began to gel, causing the viscometer reading to increase. When the temperature reached approximately 50°C, the viscometer reading had increased above the maximum scale reading of 2560 mPa•s.

EXAMPLE 35SHORTENING

<u>Ingredients</u>	<u>Weight Percent</u>
Freeze-dried protein-emulsifier complex prepared according to Example 20	15.0
Wesson canola oil	<u>85.0</u>
	100.0

With stirring in a Waring® blender at low speed, the protein-emulsifier complex was added to the canola oil. The mixture was blended at medium speed for 2 minutes, then transferred to a beaker, heated to 80°C with stirring, and cooled to 5°C in a refrigerator. After 24 hours, the mixture had the appearance and consistency of shortening.

EXAMPLE 36GELATION OF VEGETABLE OIL WITH A COMPLEX OF CASEINATE,STEARIC ACID, AND DIACETYLTARTARIC ACID ESTERS OF MONOGLYCERIDES

With stirring in a Waring® blender at low speed, 7.5 grams of spray-dried protein-emulsifier complex prepared according to Example 22 was added to 42.5 grams of Wesson canola oil. The mixture was blended at medium speed for 2 minutes. A portion was transferred to a Searle type viscometer with programmable temperature controller, and apparent viscosity was monitored at a continuous shear rate of 132 sec<sup>-1</sup>. Initial viscosity at 25°C was 156 mPa•s. The sample was heated to 85°C, then cooled. During cooling, the sample began to gel, causing the viscometer reading to

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increase. When the temperature reached approximately 50°C, the viscometer reading had increased above the maximum scale reading of 2560 mPa•s.

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CLAIMS

1. A composition comprising an ionic complex formed from at least one ionizable emulsifier, or salts thereof, and one or more substances selected from the group consisting of ionizable polypeptides, salts thereof, ionizable hydrocolloids and salts thereof, with the proviso that if the charges on said emulsifier, polypeptide and hydrocolloid are of the same sign said complex is formed in the presence of a cross-linking agent.

2. The composition of claim 1 wherein the charges on said emulsifier, ionizable polypeptide and hydrocolloid are positive and said cross-linking agent is a polyvalent anion or precursor therefor or wherein the charges on said emulsifier, ionizable polypeptide, and hydrocolloid are negative and said cross-linking agent is a polyvalent cation or precursor therefor.

3. The composition of claim 2 wherein said polyvalent anion is selected from the group consisting of  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , borates, poly(sulfonato) organic compounds, poly(sulfato) organic compounds, poly(phosphonato) organic compounds, poly(phosphato) organic compounds, poly(carboxyl) compounds; precursors thereof; and combinations thereof or wherein said polyvalent cation is selected from the group consisting of polyvalent cations of elements of groups II and III, of the Periodic Table, transition metals and polyammonium compounds, and combinations thereof.

4. The composition of claim 1 further comprising at least one pH adjusting agent.

5. The composition according to claim 1 further comprising an aqueous dispersion medium.

6. The composition of claim 1 wherein  
a) said emulsifier is selected from the group consisting of ionizable group containing esters of fatty acids with polyhydroxy compounds, ionizable group containing esters of fatty alcohols with acids selected from the group consisting of polycarboxylic, poly(sulfato), poly(sulfonato), poly(phosphato) and poly(phosphonato) acids, lecithin and derivatives thereof; fatty acids; and combinations thereof;

b) said polypeptide is selected from the group consisting of milk proteins, animal proteins, vegetable proteins; derivatives thereof; and combinations thereof; wherein said protein is selected from the group consisting of casein, whey protein concentrate, sweet dairy whey, gelatin, gelatin hydrolyzates and succinylated gelatin;

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and c) said hydrocolloid is selected from the group consisting of carrageenan, alginic acid, agar, gum arabic, gum tragacanth, xanthan gum, gellan gum, furcellaran, carboxymethylcellulose, pectin, modified food starches and chitosan; and combinations thereof.

5           7. The composition of claim 6 wherein said emulsifier is selected from the group consisting of diacetyl tartaric acid esters of mono- and diglycerides, lactyl esters of fatty acids, lactylated fatty acid esters of glycerol and propylene glycol, glyeryl-lacto esters of fatty acids, lactyl stearates, sodium stearyl fumarate, citric acid esters of monoglycerides, succinic acid esters of monoglycerides, lecithin, hydroxylated lecithin, 10 monosodium phosphate derivatives of mono- and diglycerides, carboxyl terminated esters of fatty acids and fatty alcohols with polycarboxylic acids, and saturated or unsaturated fatty acids.

8. The composition of claim 1 further comprising an edible fat or oil wherein said fat or oil is selected from the group consisting of vegetable fats and oils, 15 animal fats and oils, anhydrous milkfat, hydrogenated vegetable oils, partially hydrogenated vegetable oils; and combinations thereof.

9. The composition of claim 8 wherein at least a portion of said fat or oil is replaced by a fat mimetic wherein said fat mimetic is selected from the group consisting of polyol fatty acid esters, e.g., sugar fatty acid esters, polyglycerol fatty acid esters; and fatty acid esters of epoxide-extended polyols, fatty acid/fatty alcohol 20 carboxy/carboxylate esters, polysiloxanes, polyoxyalkylene fatty acid esters, fatty alcohol esters of polycarboxylic acids, e.g., malonic acid, fatty alcohol diesters, alkyl malonic acid fatty alcohol diesters and dialkyl malonic acid fatty alcohol diesters; alkyl glycoside fatty acid polyesters, alpha-acylated fatty acid triglycerides, glycerol fatty 25 alcohol diethers, monoglyceride fatty alcohol diethers, and glycerol esters of alpha-branched carboxylic acids, diol lipid analogues, poly(vinyl alcohol) fatty acid esters, tris(hydroxymethyl)alkyl esters of fatty acids and dicarboxylate extended fatty acid derivatives, cycloalkyldiol esters, primary amide esters, amide/ether/ester derivatives, complex linked esters, and triglycerides esterified at the 1- and 3-positions with 30 saturated long chain fatty acids and at the 2-position with a short chain acid.

10. The composition of claim 1 further comprising a gel-forming composition wherein said gel-forming composition is selected from the group consisting of agar, gelatin, pectins, xanthans, alginates, locust bean gum, guar gum, konjac flour and carrageenans and combinations thereof or a mixture comprising an



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alginate, xanthan, carrageenan or succinoglycan and at least one cross-linking agent; and further comprising at least one acidic pH adjusting agent wherein said pH adjusting agent is an acid selected from the group consisting of phosphoric, lactic, fumaric, adipic, malic, tartaric, aconitic, citric, and sulfuric acid; salts thereof; acetic and hydrochloric acids, glucono delta lactone; and combinations thereof.

11. The composition of claim 1 further comprising at least one additive selected from the group consisting of flavorants, colorants, sweeteners, fat extenders wherein said fat extenders are selected from the group consisting of dextrans, maltodextrans, modified starches, microcrystalline cellulose, polydextrose, inulin, microparticulated proteins, microparticulated carbohydrates and combinations thereof. mouthfeel agents and salts.

12. A composition comprising an ionic complex formed from at least one ionizable emulsifier and one or more substances selected from the group consisting of ionizable polypeptides and ionizable hydrocolloids; and salts thereof; with the proviso that if the charges on said emulsifier, polypeptide and hydrocolloid are of the same sign said complex is formed in the presence of a cross-linking agent wherein said complex is prepared by

a) admixing said emulsifier and an aqueous solution of said polypeptide and/or hydrocolloid and said crosslinking composition, if present, and b) heating and stirring the above mixture until any precipitate formed in a) disperses in the aqueous medium to form a dispersion.

13. The composition of claim 12 wherein the viscosity and/or opacity thereof is raised to a desired level by adjusting the pH of the dispersion wherein the adjusted pH is in the range from about 6 to about 8.

14. The composition of claim 12 wherein said preparation further comprises drying the dispersion of step b).

15. The composition of claim 13 wherein said preparation further comprises drying the pH adjusted dispersion.

16. A foodstuff comprising the composition of claim 1 wherein said foodstuff is selected from the group consisting of spreads, margarines, shortenings, frozen desserts, salad dressings, dips for crackers, dips for chips, dips for vegetables, confections having normally present triglycerides, whipped toppings, frostings, fillings for cakes, fillings for cookies, whipped desserts, gelled desserts, puddings, beverages, soups, and baked goods.

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17. A process for preparing a composition, useful in preparing food products, which comprises an ionic complex formed from at least one ionizable emulsifier, and one or more substances selected from the group consisting of ionizable polypeptides and ionizable hydrocolloids, with the proviso that if the charges on said emulsifier, polypeptide and hydrocolloid are of the same sign, said complex is formed in the presence of a cross-linking agent wherein said process comprises the steps of

5 a) admixing said emulsifier, an aqueous solution of said polypeptide and/or hydrocolloid, or salts thereof and said crosslinking composition, if present; and b) heating and stirring said mixture until any precipitate formed therein disperses in the aqueous medium.

18. The process of claim 17 further comprising the steps of a) treating the dispersion with a pH adjusting composition until the viscosity and opacity of the mixture is raised to a desired level wherein said pH adjusting composition is a base selected from the group consisting of alkali and alkaline earth metal hydroxides, carbonates, acid carbonates and phosphates; or said pH adjusting agent is an acid selected from the group consisting of phosphoric, aconitic, lactic, fumaric, adipic, malic, tartaric, citric, and sulfuric acids; salts thereof; acetic and hydrochloric acids; glucono-delta-lactone; and combinations thereof and b) drying said dispersion.

19. The process of claim 17 further comprising admixing an aqueous solution of a gel-forming composition at an elevated temperature.

20. The process of claim 17 further comprising the step of adding at least one additive selected from the group consisting of flavorants, colorants, sweeteners, fat extenders wherein said fat extenders are selected from the group consisting of dextrins, maltodextrins, modified starches, microcrystalline cellulose, polydextrose, microparticulated proteins and microparticulated carbohydrates; and combinations thereof; mouthfeel agents and salts to the product of step (b).

21. The process of claim 17 comprising the further step of adding an edible fat or oil to the product of step (b) wherein at least a portion of said fat or oil may be replaced by a fat mimetic wherein said fat mimetic is selected from the group consisting of sugar fatty acid esters, polyol fatty acid esters, polyglycerol fatty acid esters, fatty acid/fatty alcohol carboxy/carboxylate esters, fatty acid esters of epoxide-extended polyols, polysiloxanes, polyoxyalkylene fatty acid esters, fatty alcohol esters of polycarboxylic acids, malonic acid fatty alcohol diesters, alkyl malonic acid fatty alcohol diesters, dialkyl malonic acid fatty alcohol diesters, alkyl glycoside fatty acid polyesters,

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alpha-acylated fatty acid triglycerides, glycerol fatty alcohol diethers, monoglyceride fatty alcohol diethers, glycerol esters of alpha-branched carboxylic acids, diol lipid analogues, poly(vinyl alcohol) fatty acid esters, tris(hydroxymethyl)alkyl esters of fatty acids, dicarboxylate-extended fatty acid derivatives, cycloalkyldiol esters, primary amide  
5 esters, amide/ether/ester derivatives, complex linked esters, triglycerides esterified at the 1- and 3-positions with saturated long chain fatty acids and at the 2-position with a short chain acid; and combinations thereof.

22. A method of reducing the fat content of a food containing an edible oil or fat comprising replacing at least a portion of the normally present edible oil or fat  
10 with a composition comprising an ionic complex formed from at least one ionizable emulsifier and one or more substances selected from the group consisting of ionizable polypeptides and ionizable hydrocolloids, with the proviso that if the charges on said emulsifier, polypeptide and hydrocolloid are of the same sign said complex is formed in the presence of a cross-linking agent.

15 23. The method of claim 22 wherein said composition further comprises a)  
at least one additive selected from the group consisting of  
a) at least one pH adjusting agent;  
b) an aqueous dispersion medium;  
c) at least one an edible oil or fat wherein at least a portion of said fat or  
20 oil may be replaced by a fat mimetic;  
d) at least one gel-forming composition;  
e) at least one acidic pH adjusting agent; and  
f) the group consisting of flavorants, colorants, sweeteners, fat extenders  
and salts.

25 24. The composition according to claim 1 for use in increasing the viscosity of oils wherein said oils are, optionally, polyunsaturated oils.

25. The composition according to claim 1 for use in increasing the opacity of low fat emulsions or increasing the viscosity of emulsions wherein said emulsions are oil in water emulsions or water in oil emulsions.

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<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 A23L1/035; A23L1/308		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	A23L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP,A,0 238 330 (THE BRITISH FOOD MANUFACTURING INDUSTRIES RESEARCH ASSOCIATION) 23 September 1987 cited in the application see claims 1-14 see page 3, line 4 - line 26 see table 1 see page 5, line 64 - page 6, line 7 see page 11, line 51 - line 59 see page 12, line 35 - page 13, line 8 --- -/--	1,5-8, 12,13, 16,17,21
<sup>10</sup> Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu- ments, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
23 JUNE 1993	0 8. 17. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	VUILLAMY V.M.L.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	<p>DATABASE WPIL  Section Ch, Week 8810, 10 February 1988  Derwent Publications Ltd., London, GB;  Class D11, AN 88-069136  cited in the application  see abstract  &amp; Research Disclosure, 20 January 1988  (GRINSTED), Abstract No. 286042</p> <p>---</p>	1,6,7, 12,16,22
X	<p>EP,A,0 086 032 (GENERAL FOODS)  17 August 1983  cited in the application  see claims 1-10  see page 2, line 28 - page 4, line 10  see examples</p> <p>---</p>	1,4-8, 11-18,20
X	<p>CH,A,470 143 (AKTIESELSKABET  GRINDSTEDVAERKET)  31 March 1969  see claims  see column 1, line 1 - line 18  see column 4, line 8 - line 21  see page 5, line 24 - page 6, line 60  see column 7, line 53 - page 8, line 8  see example 4; table 1</p> <p>---</p>	1,6-8, 16,25
X	<p>EP,A,0 468 552 (MERCK)  29 January 1992  see claims 1-4,7  see page 2, line 57 - page 3, line 7  see page 3, line 30 - page 4, line 40</p> <p>---</p>	1,5,6,7, 10,16
X	<p>CH,A,542 590 (RIKEN VITAMIN OIL)  30 November 1973  see claims  see column 1, line 1 - line 59  see column 2, line 5 - line 19  see examples 1-3</p> <p>---</p>	1,5-8, 11,16
X	<p>US,A,3 356 507 (W.H. WINGERD)  5 December 1967  see claims 1-9  see column 1, line 25 - column 2, line 19  see examples 1-5</p> <p>-----</p>	1,5,8, 12,13,16

Form PCT/ISA/210 (extra sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9302167  
SA 71843

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 23/06/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0238330	23-09-87	None	
EP-A-0086032	17-08-83	US-A- 4411926	25-10-83
CH-A-470143	31-03-69	BE-A- 658245	30-04-65
		DE-A, B 1719418	03-06-71
		GB-A- 1082283	
		NL-A- 6500245	14-07-65
EP-A-0468552	29-01-92	CA-A- 2043764	07-12-91
		JP-A- 4252134	08-09-92
CH-A-542590	30-11-73	None	
US-A-3356507		None	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82